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CALCIUM FLUORIDE CRYSTAL, MANUFACTURE OF THE SAME AND PROJECTION
EXPOSURE DEVICE USING THE SAME

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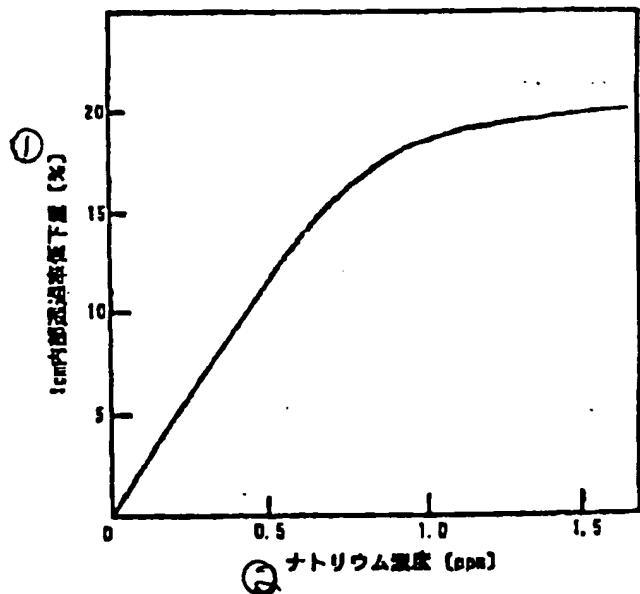
Abstract

Objective

To obtain a calcium fluoride crystal, with excellent resistance to ArF excimer lasers, that can be used in optical systems having ArF excimer lasers as light sources.

Means

In the Bridgman method, the sodium content in the calcium fluoride crystal is suppressed to 0.2 ppm or less by means of precisely controlling the lowering rate and temperature conditions.



Key: 1 Decrease in transmittance in 1 cm (%)
2 Sodium concentration (ppm)

Claims

1. A calcium fluoride crystal used in optical systems having excimer lasers as light sources, said calcium fluoride crystal being characterized in that the amount of sodium contained in said crystal is 0.2 ppm or less, and the decrease in transmissivity is 5% or less per 1 cm of

thickness when irradiated with 10^4 pulses or more from an ArF excimer laser at an energy density of 100 mJ/(cm²·pulse).

2. A method for manufacturing calcium fluoride crystal used in optical systems having excimer lasers as light sources, said method for manufacturing calcium fluoride crystal comprising a pretreatment process wherein a high-purity calcium fluoride raw material and a scavenger are mixed in a crucible in an evacuated heated furnace, thus bringing about deoxygenation reactions, and after melting the aforementioned reaction product at a temperature that is no less than the melting point of calcium fluoride, the crucible is lowered at a rate of 5 mm/h or less, and the aforementioned reaction product is gradually made to crystallize from the bottom, thereby producing a pretreatment product, and a growing process wherein the aforementioned pretreatment product is melted at a temperature that is no less than the melting point of calcium fluoride in an evacuated heated furnace, whereupon the crucible is lowered at a rate of 1 mm/h or less, thus causing the aforementioned pretreatment product to gradually crystallize from the bottom of the crucible, producing a calcium fluoride crystal with a sodium content of 0.2 ppm or less.

3. The method for manufacturing calcium fluoride crystal according to Claim 2, said method for manufacturing calcium fluoride crystal being characterized in that, after cutting away the uppermost section of the pretreatment product obtained in the pretreatment process, the pretreated product is used in the growing process.

4. A projection exposure device, characterized by being a device for projecting and exposing the pattern image of a mask on a substrate using an optical projection system, characterized by comprising an optical illumination system, for illuminating the mask, using an excimer laser as the exposure light source, and an optical projection system, that forms the pattern image of the aforementioned mask on the substrate, which contains a calcium fluoride crystal optical member having a sodium content of 0.2 ppm or less.

5. A projection exposure device, characterized by being a device for projecting and exposing a pattern image of a mask on a substrate using an optical projection system, characterized by comprising an optical illumination system, that illuminates a mask, using an excimer laser as the exposure light source, and contains a calcium fluoride crystal optical member with a sodium content of 0.01 ppm or less, and an optical projection system that forms the aforementioned mask pattern image on the substrate.

6. The projection exposure device described in Claim 4 or Claim 5, said projection exposure device being characterized in that the optical illumination system and/or optical projection system contains a calcium fluoride crystal optical member and quartz glass.

Detailed description of the invention

[0001]

Technical field of the invention

The present invention concerns a calcium fluoride crystal used as a transmissive optical member such as a lens, prism or window in optical systems having excimer lasers, particularly ArF excimer lasers, as light sources. In addition, the present invention concerns a projection exposure device that has an excimer laser, particularly an ArF excimer laser, as its light source.

[0002]

Prior art

Excimer lasers can oscillate with high power and high frequency in a wavelength range extending from ultraviolet to vacuum ultraviolet. Research and development, as well as implementation, are being carried out concerning the use of these lasers as high-efficiency, short-wavelength pulsed light sources. In recent years, expansion has been seen, particularly in regard to the use of these lasers as light sources for ultra-fine detailed lithography by employing their property of having a short wavelength.

[0003]

In lithographic processes, a method is primarily used wherein a pattern that has been drawn on a mask is transferred onto a wafer using a laser. These methods are referred to as photolithography. In general, the resolution of the transferred pattern increases in proportion to the aperture of the lens and the inverse of the wavelength of the light. However, there are manufacturing limitations with regard to the lens aperture, and thus shortening the wavelength of the light is an effective means to increase resolution. To this end, wavelengths have been shortened by using γ -radiation (436 nm) and i-radiation (365 nm), or by using KrF excimer lasers (248 nm) as light sources for photolithography. It has been confirmed that a resolution of 0.28 μm has been realized with reduction projection exposure devices that employ KrF excimer lasers as light sources, and a development level of 0.25 μm is being achieved.

[0004]

There are devices in which KrF excimer lasers, or light with a wavelength that is even shorter than excimer laser light, are used as light sources, specifically, light with a wavelength of 200 nm or less, referred to as the vacuum ultraviolet range light. It is generally assumed that synthetic quartz glass that can be ground to a large aperture and that has low absorption can be used for optical members in these devices. In addition, other known transmissive crystal materials include lithium fluoride crystal, magnesium fluoride crystal and calcium fluoride

crystal. However, lithium fluoride crystal is extremely deliquescent and cannot be polished, so it is impractical to use this material due to problems with handling. Moreover, magnesium fluoride has biaxial crystals, and thus has optical anisotropy and exhibits birefringence phenomena. For this reason, the material can be used in optical members for which a high objective capacity is not required, such as polarizing prisms and other polarizing elements that employ a birefringence phenomenon, or in vacuum system windows. However, this material is unsuitable for use as an optical material for which high objective performance is required, as with lenses and prisms used in photolithography. Calcium fluoride crystal does not exhibit deliquescence or optical anisotropy, and is a material that has excellent transmissivity with respect to ultraviolet light. The material is thus looked upon favorably in terms of its capacity for use in precision optical systems.

[0005]

Conventional calcium fluoride crystal has good durability in terms of transmittance when exposed to KrF excimer laser light. In other words, the material has good resistance to KrF excimer lasers, and can be used in optical systems wherein strong KrF excimer lasers are used as light sources. This fact has already been described in *Applied Optics*, Vol. 31, no. 28/6062-6075/(1992).

[0006]

Problems to be solved by the invention

Calcium fluoride crystals have a short wavelength absorption terminus at 124 nm, and are materials that have good transmissivity in the short wavelength range ranging from ultraviolet to vacuum ultraviolet light. For this reason, calcium fluoride crystals that have been used in optical systems with 248-nm KrF excimer lasers as light sources are considered easy because they can be used without modification in optical systems having 193-nm ArF excimer lasers as light sources. However, calcium fluoride crystals that are illuminated with ArF excimer lasers having a high energy density undergo an extreme decrease in transmittance. Specifically, assuming that the energy density used with optical systems in reduction projection exposure devices is a maximum of about $100 \text{ mJ}/(\text{cm}^2 \cdot \text{pulse})$, conventional calcium fluoride crystals have a decrease in transmittance of about 8% or more per 1 cm of thickness. In addition, a heating phenomenon occurs due to conversion of light energy into thermal energy by means of absorption, thus leading to variation in the refractive index. Such materials thus cannot be used as high-precision lenses due to slight deformation. Reduction projection exposure devices having optical systems constituted by calcium fluoride crystal have thus not been employed in devices with ArF excimer lasers as light sources.

[0007]

Means to solve the problems

In order to solve the problems described above, the present invention pertains to a calcium fluoride crystal that is used in optical systems for reduction projection exposure devices having excimer lasers as light sources, and offers a calcium fluoride crystal, wherein the amount of sodium contained in the crystal is controlled to 0.2 ppm, which has excellent capacity to withstand ArF excimer lasers, and can be used in optical systems in which ArF excimer lasers are used as light sources. The present invention also pertains to a reduction projection exposure device that employs this crystal as a transmissive member in its optical system. The present invention is characterized in that a reduction projection exposure device can be realized that employs an ArF excimer laser as a light source, which has an even shorter wavelength than KrF excimer lasers.

[0008]

Embodiment of the invention

The calcium fluoride crystal of the present invention that is used in optical systems that employ excimer lasers as light sources can be obtained by using the Bridgman method (also referred to as the Stockberger method or crucible lowering method) described below in order to precisely control the lowering rate and temperature conditions.

[0009]

With calcium fluoride crystals that are used in the ultraviolet to vacuum ultraviolet range, natural fluorite is not used as the raw material. In general, high-purity raw material obtained by chemical synthesis is used. The raw material can be used as a powder; or in order to prevent a decrease in volume when melted, partially melted material or pulverized product produced therefrom can be used. Pretreatment is carried out by mixing this raw material with a fluoride scavenger.

[0010]

The pretreatment is a process that is carried out in order to obtain a high-purity pretreated product, and by this means, staining of the growing device can be prevented, and a high-purity calcium fluoride crystal can be obtained in the subsequent growing process. The high-purity calcium fluoride raw material and the scavenger are mixed and loaded into a pretreatment crucible, which is placed in an evacuated heated furnace, whereupon the material is melted under a deoxygenated atmosphere inside the device. At this time, the evacuated atmosphere is

maintained at 10^{-5} to 10^{-6} Torr in order to eliminate oxides and volatile impurities (reaction products). The temperature of the device is then gradually increased, and deoxygenation reactions are brought about by maintaining the material at a temperature at which the scavenger and raw material react. After increasing the temperature to above the melting point of the raw material, the temperature is then gradually decreased in order to solidify the melt, thus producing a pretreated product.

[0011]

Next, crystal growth is carried out. The crucible that is packed with the aforementioned treated product is placed in a calcium fluoride growing device, and the interior of the growing device is maintained in an evacuated atmosphere at 10^{-5} to 10^{-6} Torr. The device temperature is then gradually increased, and the pretreated product is melted at a temperature that is greater than the melting point of calcium fluoride. In the crystal growing stage, the crucible is lowered; and by this means, crystallization is made to occur gradually from the bottom of the crucible. The grown crystal (ingot) is prevented from cooling rapidly, and simple cooling is allowed to occur. The residual stress is extremely large as a result of this process, and the ingot is thus subjected to thermal treatment. The ingot that has been obtained in this manner is then cut and processed to obtain the calcium fluoride crystal optical member.

[0012]

The calcium fluoride crystal that is obtained in the present invention is used in optical systems having excimer lasers as light sources. Good initial transmittance (transmittance prior to laser irradiation) is desired of the calcium fluoride of the present invention. For example, with an optical lens for a stepper wherein an ArF excimer laser is used as a light source, a value of 99.8% or greater is desired for the transmittance per 1 cm (transmittance excluding loss due to reflection of a sample with a thickness of 1 cm).

[0013]

In addition, because the excimer laser is a high-power pulse laser with a short wavelength, low optical characteristic modification related to transmittance and other characteristics, or good resistance to excimer lasers is desired when the calcium fluoride crystal of the present invention that is used is irradiated with the laser. When an alkali metal is admixed as monovalent cations in the calcium fluoride crystal, the ions insert into the calcium sites, and readily form color centers due to charge compensation. In short, defects, produced due to the admixture of alkali metal, form color centers that have absorption ranges that are in the visible

range when irradiated with ArF excimer laser, and these absorption ranges cause a reduction in transmittance at 193 nm.

[0014]

The color center concentration and the coefficient of absorption due to intrinsic absorption resulting therefrom are considered to be proportional to each other.

[0015]

Formula 1

$$T = I/I_i = \exp(-aNd) \quad (1)$$

[0016]

Herein, T denotes the transmittance, I_i denotes the energy density of the incident light, I denotes the energy density of the transmitted light, a denotes a constant, N denotes the color center concentration, and d denotes the thickness of the measured sample. When the amount of decrease in transmittance is small ($T \sim 1$), assuming:

[0017]

Formula 2

$$\Delta T = (I_i - I)/I_i$$

[0018]

then the following formula results:

[0019]

Formula 3

$$\Delta T \sim aNd \quad (2)$$

[0020]

Consequently, the color center concentration and the decrease in transmittance stand in a proportional relationship. When the sodium impurity content is extremely small, the absorption due to the color centers appears at about 325 nm. As the sodium content increases, the absorption amount also increases, and absorption appears in the vicinity of 385 nm or 600 nm. As the concentration increases further, absorption at 325 nm does not increase (Figure 2). This is

thought to be because the type of color center changes and the absorption band changes in accordance with the sodium content.

[0021]

Of the three absorption bands, the absorption occurring at 325 nm is the absorption that has an effect on transmittance at 193 nm. Consequently, if the sodium content is decreased to below the threshold value, an extremely large influence on transmittance at 193 nm is seen. The inventors of the present invention et al. determined the threshold value for the sodium content at approximately 1 ppm. Consequently, Formula 2 is established for the concentration decrease.

[0022]

Measurement of sodium concentration in the calcium fluoride crystal of the present invention was carried out by activation analysis, which can be used in the analysis of trace quantities. Activation analysis is a method wherein stable atomic nuclei in the target molecules are broken down by irradiation with neutrons, thus producing unstable isotope elements, and the radiation produced from the atomic nuclei is measured in order to attain reliable quantitative analysis. In most other analytical methods, the change in energy or state of electron groups is measured, but the chemical condition is readily influenced by the pretreatment condition of the example. However, activation analysis is characterized in that the chemical state of the material has no effect because the atomic nuclei are acted upon directly.

[0023]

The calcium fluoride of the present invention was used as a sample, and was subjected to ArF excimer laser resistance testing, by carrying out irradiation testing using an ArF excimer laser. It was found that the change in transmittance of the calcium fluoride crystal is dependent on the energy density of the light that is used for irradiation, and that there was no relationship to shot number. Thus, an irradiation energy density of $100 \text{ mJ}/(\text{cm}^2 \cdot \text{pulse})$ and an irradiation pulse number of 10^4 were used. A small decrease in transmittance due to irradiation at 193 nm indicated good ArF excimer laser resistance.

[0024]

The decrease in transmittance with an ArF excimer laser wavelength of 193 nm was measured with a spectral photometer (CARY5, manufactured by Varian), and was 0.1% or less for a thickness of 1 cm. In other words, the transmittance was 99.9% or greater per 1 cm of thickness. The calcium fluoride crystal of the present invention, even when irradiated with an

ArF excimer laser, showed no decrease in transmittance, thereby confirming that the material was calcium fluoride crystal having excellent resistance to ArF excimer lasers.

[0025]

Moreover, ArF excimer laser testing was carried out with conventional calcium fluoride crystal and calcium fluoride crystal containing different amounts of sodium, and by this means, a strong relationship was indicated between the amount of sodium contained and ArF excimer laser resistance. The results are shown in Figure 1. Considering Figure 1 and the proportional relationship between transmittance decrease and energy density strength, the following formula can be derived taking the transmissivity decrease per 1 cm thickness as Y%, taking the energy density as $E \text{ mJ}/(\text{cm}^2 \cdot \text{pulse})$, and taking the sodium concentration as [Na] ppm.

[0026]

Formula 4

$$Y=0.25E[\text{Na}] \quad (3)$$

[0027]

The energy density for ArF excimer laser has a practical maximum of 100 $\text{mJ}/(\text{cm}^2 \cdot \text{pulse})$, and when a transmittance of 99.8% per 1 cm of thickness in the calcium fluoride crystal is taken to be required of an optical member, an appropriate value for the sodium content, as determined based on formula (3) is 0.008 ppm. The energy density of an ArF excimer laser in an objective optical system for reduction projection exposure devices has a maximum of 4 $\text{mJ}/(\text{cm}^2 \cdot \text{pulse})$, and with an optical member that requires a transmittance of 99.8% or greater per 1 cm of thickness of the calcium fluoride crystal, an appropriate value for the sodium content based on Formula 3 is 0.2 ppm.

[0028]

KrF excimer laser resistance testing was also carried out with calcium fluoride crystals having different sodium contents. The irradiation density was 400 $\text{mJ}/(\text{cm}^2 \cdot \text{pulse})$ and the irradiation pulse number was 10^4 . With all of the samples, there was no decrease in transmittance, and it was confirmed that there was no dependence on sodium concentration. With a method wherein crystallization was carried out by hardening a melt according to the Bridgman method, the impurity concentration C_S entering the crystal from the melt was generally smaller than the similar impurity concentration C_L in the melt. The impurity atoms that do not enter into the crystal are extracted from the melt that is in contact with the solid-liquid interface. The impurity concentration C_0 at the solid-liquid interface is determined by an equilibrium between

this extraction and elution of impurity atoms to the side of the melt due to the concentration gradient. Consequently, the distribution of impurity concentration C occurs according to the diffusion equation (4).

[0029]

Formula 5

$$D_L(d^2C/d\zeta^2) + V(dC/d\zeta) = 0 \quad (4)$$

[0030]

Herein, D_L denotes the diffusion coefficient, V denotes the growth rate, ζ denotes the coordinate in the direction of growth with the origin fixed at the solid-liquid interface. The boundary conditions are as follows.

[0031]

Formula 6

$$C(\delta) = C_L \quad (5)$$

$$-D_L(dC/d\zeta)_{\text{interface}} = V(C_0 - C_s) \quad (6)$$

[0032]

Herein, d is the thickness of the impurity diffusion layer.

Using the equilibrium segregation coefficient k defined in formula (7), formula (8) is derived in order to analyze the solid-liquid interface, and formula (9) is obtained by determining the effective segregation coefficient K .

[0033]

Formula 7

$$C_s = kC_0 \quad (7)$$

$$\zeta \rightarrow 0 \quad (8)$$

$$K = C_s/C_L = k/(k + (1-k)\exp(-V\delta/D_L)) \quad (9)$$

[0034]

In order to reduce the growth rate V in formula (9), the effective segregation coefficient is reduced, and this has the effect of reducing the impurity concentration C_s introduced into the crystal. However, if the crystal growth rate is greatly reduced in order to reduce the impurity concentration entering into the crystal, it will require an extremely long period of time in order to

crystallize all of the melt. During growth of conventional calcium fluoride crystals, the primary objective is to inhibit production of absorption bands for which bubbles, impurities, and lead are taken as factors. Consequently, crystallization ordinarily is carried out at about 2 mm/h because it is not necessary to pay extremely close attention to the growth rate. This is because the presence of trace amounts of specific impurities is not as much of an issue as in the present invention.

[0035]

The inventors of the present invention et al., in growing the calcium fluoride crystal, carried out a pretreatment prior to the growth stage to obtain a high-purity pretreated product. This product was then used as raw material for growing, thus producing a calcium fluoride crystal. During the pretreatment stage and the growing stage, the growth rate, or the rate of lowering of the crucible, was optimized. By this means, the amount of impurities entering into the crystal was reduced, and it was discovered that it was thereby possible to grow calcium fluoride crystals with good efficiency.

[0036]

Specifically, the method for manufacturing calcium fluoride crystal of the present invention comprises a pretreatment process wherein a high-purity calcium fluoride raw material and a scavenger are mixed in a crucible in an evacuated and heated furnace, thus bringing about deoxygenation reactions. After melting the aforementioned reaction product at a temperature that no less than the melting point of calcium fluoride, the crucible is lowered at a rate of 5 mm/h or less, and the aforementioned reaction product is gradually made to crystallize from the bottom, thereby producing a pretreatment product. The invention also comprises a growing process wherein the aforementioned pretreatment product is melted, at a temperature that is no less than the melting point of calcium fluoride, in an evacuated heated furnace, whereupon the crucible is lowered at a rate of 1 mm/h or less, thus causing the aforementioned pretreatment product to gradually crystallize from the bottom of the crucible, producing a calcium fluoride crystal with a sodium content of 0.2 ppm or less.

[0037]

From Formula (8) above, by means of decreasing the impurity concentration C_L in the melt and by holding the effective segregation coefficient K constant, it is clear that the impurity concentration C_s introduced into the crystal can be decreased. This can be taken as an effective method because it allows for the selective production of determinate physical properties. During actual crystal growing, the calcium fluoride crystal of the present invention is grown while providing a good balance between the selection of optimal growing rate and the decrease in

concentration of sodium, which is a specific physical property in the melt, while not skewing the balance towards either process.

[0038]

In consideration of the fact that the impurity concentration in the melt increases with crystallization, the initial impurity concentration C_{L0} in the melt and the crystallization ratio g are expressed by well-known formula (10).

[0039]

Formula 8

$$C_s = KC_{L0}(1-g)^{(K-1)} \quad (10)$$

[0040]

From formula (10), it can be predicted that the impurity concentration C_s in the crystal will increase in conjunction with growth, but by means of research and development concerning calcium fluoride crystal growth by means of the vertical Bridgman method that is most commonly used, the inventors of the present invention discovered that when the crystallization ratio g is greater than 0.95, the impurity concentration in the crystal increases dramatically in the final stage of crystallization. The calcium fluoride crystal of the present invention thus was grown while employing this phenomenon in order to decrease the concentration of sodium.

[0041]

The calcium fluoride crystal of the present invention is obtained by the method described above, and because the amount of sodium is decreased relative to past materials, the excimer laser resistance is greatly increased. The exposure device of the present invention is described below. The present invention is used specifically in a projection exposure device referred to as a stepper, which is used in order to project a pattern image from a reticle onto a wafer coated with a photoresist. The basic structure of the exposure device pertaining to the present invention is shown in Figure 3. As shown in Figure 3, the exposure device of the present invention comprises at least a wafer stage (3) where a substrate (W) that is coated with photosensitive agent is placed on a surface (3a), an optical illumination system (1) that performs illumination using vacuum ultraviolet light of a specific wavelength as the illumination light, thereby transferring the prepared pattern of the mask (reticle R) onto the substrate (W), a light source (100) that supplies exposure light to the optical illumination system (1), and an optical projection system (5) that is located between a second surface (image surface) that corresponds to the surface of the substrate (W) and an initial surface (P1) (object surface) on which the mask (R) is provided in order that

the image of the pattern of mask (R) can be projected onto the substrate (W). The optical system (1) for illumination includes an optical alignment system (110) for adjusting the relative location between the mask (R) and wafer (W), where the mask (R) is arranged on the reticle stage (2) so that it can be moved parallel with respect to the surface of the wafer stage (3). The reticle exchange system (200) transports and exchanges the reticle (mask R) that has been placed on the reticle stage (2). The reticle exchange system (200) includes a stage driver for moving the reticle stage (2) parallel with respect to the surface (3a) of the wafer stage (3). The optical projection system (5) has an optical alignment system that is used in scan-type exposure devices.

[0042]

Thus, the exposure device of the present invention is a device that employs an optical member (for example, an optical lens), composed of calcium fluoride crystal having a reduced sodium content, manufactured by the method of the present invention described above. Specifically, the exposure device of the present invention shown in Figure 3 can be equipped with the optical lens pertaining to the present invention, which is used as the optical lens (10) for the optical projection system (5) and/or the optical lens (9) of the optical illumination system (1).

[0043]

When the calcium fluoride crystal of the present invention is used in the optical illumination system, it is desirable to use a material wherein the sodium content is 0.01 ppm or less. When used in the optical projection system, on the other hand, it is preferable to use a material wherein the sodium content is 0.2 ppm or less. Because the optical illumination system is close to the light source, the lens is irradiated with light of a comparatively short light flux, so the energy density is high, which increases the amount of incurred damage. Consequently, the aforementioned material is used because additionally high resistance to ArF excimer lasers is desired.

[0044]

As described above, the exposure device of the present invention employs calcium fluoride crystal that has been endowed with resistance to ArF excimer lasers by virtue of its decreased sodium content. Consequently, ArF excimer lasers that have been considered impossible to use in the past can now be used for exposure light. In addition, by means of using quartz glass along with the calcium fluoride crystal of the present invention, it is possible to correct for various types of aberrations such as a chromatic aberration by using the difference in refractive index and dispersion of these materials.

[0045]

An example of a method for producing the calcium fluoride crystal of the present invention is described below. In the first stage, a pretreatment is carried out with the objective of purifying the raw material. As has been known in the past, the oxygen content is a physical property that should be given attention, but the most important physical attribute pertaining to the present invention relates to sodium. The pretreatment device is a vacuum heating device whereby the vertical Bridgman method can be carried out. A carbon vessel that has been processed to a high purity is placed in the pretreatment device, and the interior of the aforementioned treatment device is evacuated to 10^{-6} Torr with an oil diffusion pump that is equipped with a liquid nitrogen cold trap. The pretreatment device is equipped with a heater that can effect resistance heating in the heating stage, and thus PID regulation is possible for the device temperature. The temperature is gradually increased, and when a temperature of 1550°C is reached, which is at least 100°C, higher than the maximum temperature in the growing process (second stage), the device is maintained at this temperature for 120 h, and is then allowed to cool to room temperature. The cleaning performed by this thermal treatment is referred to as baking. Baking has the effect of cleaning the entire inside region of the aforementioned pretreatment device, including, in addition to the carbon vessel, the heater and the thermal insulating material. The evacuation level during the period when the temperature decreases to room temperature is preferably 10^{-7} Torr.

[0046]

Next, high-purity lead fluoride powder is added in the amount of 0.1 mol% with respect to the high-purity calcium fluoride raw material powder, and after stirring the substances well, the material is loaded into a clean carbon vessel that has been baked. After placing the carbon vessel at the prescribed location in the pretreatment device, the device is evacuated to 10^{-6} Torr. The material is then gradually heated, and deoxygenation reactions are allowed to occur for 24 h at 900°C. The deoxygenation reactions occur according to the formula

$\text{CaO} + \text{PbF}_2 \rightarrow \text{CaF}_2 + \text{PbO} \uparrow$. The temperature increase is continued, and after melting at 1420°C, the temperature is maintained for 24 h in order to make the viscosity and composition of the melt uniform. Crystallization is then initiated by lowering. The rate of lowering of the carbon crucible, or the growing rate, is maintained at 3 mm/h up to the point at which all of the melt has crystallized. Once the sequence of the pretreatment process has been completed, a 15-mm thickness of the upper region of the ingot that has a comparatively high concentration of sodium is removed, and the remaining ingot is used as bulk raw material. Because it is not necessary to maintain the growing rate at a constant level in the area corresponding to the 15-mm thickness at the upper region of the ingot, efficiency can be improved by initiating a rapid temperature decrease. When the sodium content was measured, by activation analysis using some of the bulk

raw material as a sample, a value of 0.5 ppm or less was obtained. In the first stage, the growing rate was fast relative to the growing process at 3 mm/h, and thus it was possible to produce a large quantity of material in a short period of time.

[0047]

In the second stage, the growing process for the calcium fluoride crystal pertaining to the present invention is carried out by means of the vertical Bridgman method in an evacuated atmosphere. The bulk raw material is placed in a carbon crucible that has been cleaned by baking, and the crucible is placed in a growing device that has been baked. Upon evacuating the device to 10^{-6} Torr, temperature increase is initiated by resistance heating from the heater. The temperature is gradually increased while controlling the temperature, and upon reaching 1420°C, the melt is made uniform by maintaining this temperature for 24 h. Crystallization is then carried out by lowering at a growing rate of 1 mm/h, and upon completion of crystallization of the entire melt, the temperature is decreased to room temperature. The sodium content is measured at 0.008 ppm or less, using part of this ingot as a sample.

[0048]

An ArF excimer laser resistance test was carried out by irradiation with 10^4 pulses of ArF excimer laser at an energy density of 100 mJ/(cm²·pulse), and the decrease in transmittance was 0.2% or less per 1 cm of thickness. Specifically, the transmittance was maintained at 99.8% or greater per 1 cm of thickness. After processing the calcium fluoride crystal that had been cut from the ingot to produce a lens, it was possible to use the lens in an optical imaging system and an optical illumination system in a reduction projection exposure device having an ArF excimer laser as a light source. Because it is possible to actually produce lenses in this manner, which has been a serious problem in the past, a reduction projection exposure device can be realized that has an ArF excimer laser as its light source.

[0049]

A calcium fluoride crystal pertaining to the present invention, that can be used in projection lenses with comparatively low energy densities, can be produced by the method described below. In the first stage, a pretreatment is, of course, carried out with the objective of purifying the raw material. However, the baking hold time is changed to 8 h, and a growing rate of 5 mm/h is sufficient. Moreover, it is sufficient to remove a thickness of 10 mm from upper region of the ingot, but a thickness of 15 mm is preferred. The sodium content in the bulk raw material manufactured in this manner is 1 ppm or less. In the first stage, it is possible to carry out manufacturing with increased efficiency because a relatively fast growing rate of 5 mm/h is used.

[0050]

The growing rate in the second stage was 1 mm/h. Part of the ingot manufactured in this manner was used as a sample, and a sodium content of 0.2 ppm or less was measured. In addition, ArF excimer laser resistance testing was carried out by irradiating the material with 10^4 pulses of ArF excimer laser light at an energy density of $4 \text{ mJ}/(\text{cm}^2 \cdot \text{pulse})$, and the decrease in resistance was 0.2% or less per 1 cm or thickness. In other words, the transmittance was maintained at 99.8% or greater per 1 cm or thickness.

[0051]

A calcium fluoride crystal cut from the ingot was processed to form a lens. It was possible to use the material as an imaging lens in the optical imaging system of a reduction projection exposure device having an ArF excimer laser as a light source.

[0052]

Effect of the invention

It is possible to produce a reduction projection exposure device wherein an ArF excimer laser is used as the light source by means of the calcium fluoride crystal pertaining to the present invention. In addition, a resolution of $0.2 \mu\text{m}$ was achieved with the ArF excimer laser reduction projection exposure device pertaining to the present invention.

Brief description of the figures

Figure 1. Diagram showing the decrease in transmissivity per 1 cm of thickness at 193 nm when calcium fluoride crystals having different sodium content concentrations were irradiated with 10^4 pulses using an ArF excimer laser at an energy density of $100 \text{ mJ}/(\text{cm}^2 \cdot \text{pulse})$.

Figure 2. Graph showing the transmissivity, including reflection, per 1 cm of thickness over a wavelength range of 190-620 nm, when calcium fluoride crystals having different sodium contents were irradiated with 10^4 pulses using an ArF excimer laser at an energy density of $100 \text{ mJ}/(\text{cm}^2 \cdot \text{pulse})$.

Figure 3. Diagram showing an example of a projection exposure device wherein an optical member with decreased sodium content is used in the optical illumination system and/or optical projection system.

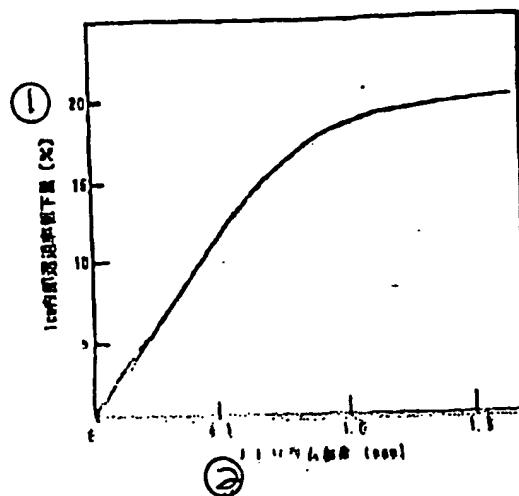


Figure 1

Key: 1 Decrease in internal transmittance per 1 cm (%)
 2 Sodium concentration (ppm)

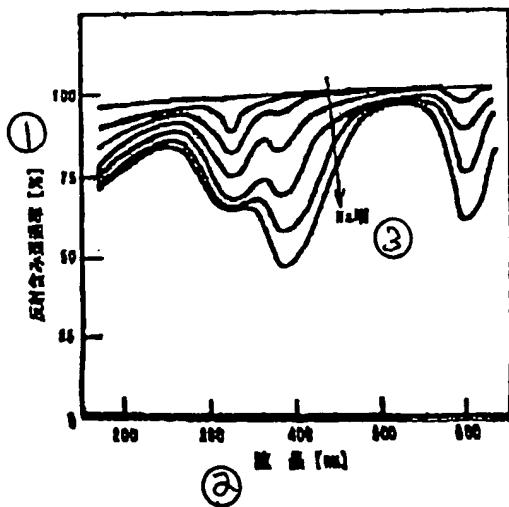


Figure 2

Key: 1 Transmittance including reflection (%)
 2 Wavelength (nm)
 3 Increasing Na

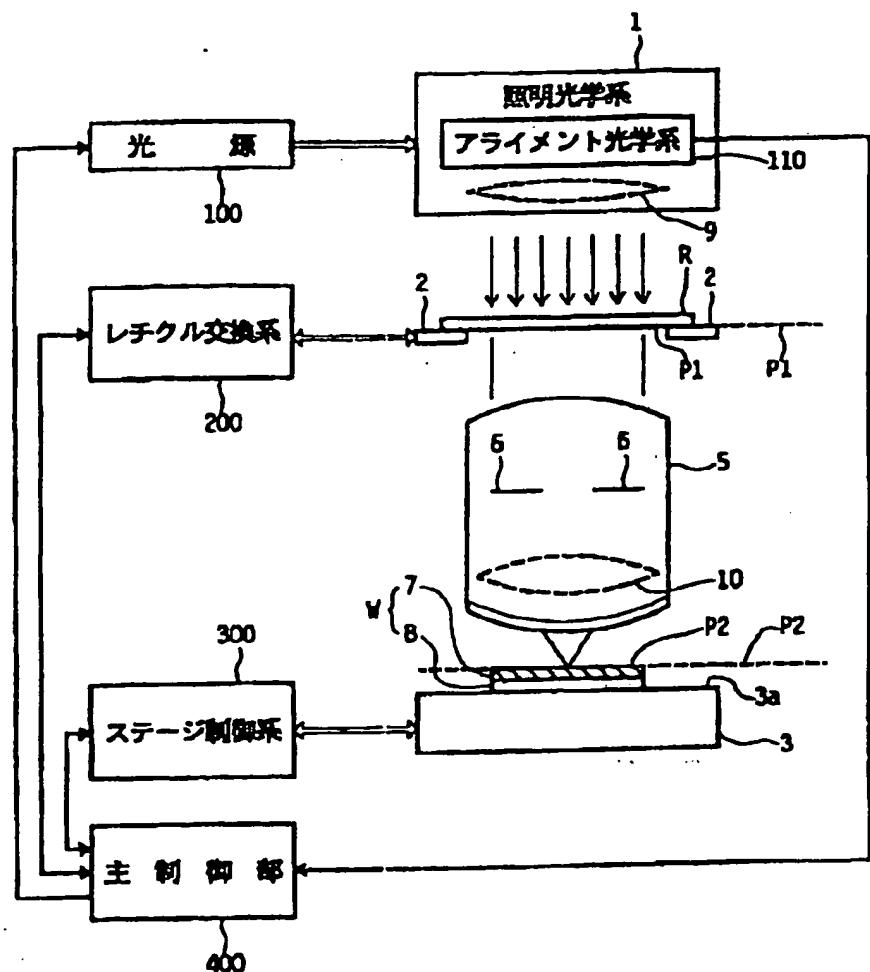


Figure 3

Key:

- 1 Optical projection system
- 100 Light source
- 110 Optical alignment system
- 200 Reticle exchange system
- 300 Stage control system
- 400 Primary controller